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DRAWINGS ATTACHED

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(54) MICROPOROUS MATERIAL

(71) We, INMONT CORPORATION, a Corporation organised under the Laws of the State of Ohio, United States of America, 1133 Avenue of the Americas, New York, New York 10036, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the manufacture of microporous sheets suitable for use as shoe upper material in place of natural leather.

According to the present invention a flexible water-vapour permeable sheet material having a microporous surface of elastomeric polyurethane carries on its surface a discontinuous pattern or an open pattern of plastic polymer containing pigment in low relief, said pattern being such that no point in said pattern is further than 2 mils from the boundary of a relief deposit of plastic polymer, and the height of said low relief pattern is not more than 1 mil. Preferably said deposited low relief polymer occupies 30 to 70% of the projected area of said pattern.

The sheet preferably carries also a higher relief pattern of spaced masses of plastic polymer with said low relief pattern being situated between said masses.

The said plastic polymer is preferably a thermoplastic elastomeric polyurethane.

The invention also extends to a process for the production of a sheet material in accordance with the invention, which comprises treating a surface of a flexible sheet material which surface consists essentially of preformed solid water vapour permeable microporous thermoplastic elastomeric polyurethane material optionally containing up to 20% by weight of other thermoplastic elastomeric polymer by contacting said surface locally with a discontinuous pattern or

an open pattern of a solution of an elastomeric polymer containing a dispersed pigment in a solvent for said polyurethane of said surface said solution containing at least 1% by weight of polyurethane in such a way that there is deposited on the said surface a discontinuous pattern or an open pattern of plastic polymer in low relief, and drying to remove the solvent by evaporation, said pattern being such that no point in said pattern is further than 2 mils from the boundary of a low relief deposit of said polymer.

The solution of elastomeric polymer preferably comprises a solution of an elastomeric polyurethane containing dispersed pigment in a solvent for said polyurethane of said surface said solution containing from 1% to 20% by weight of polyurethane and the amount by weight of said pigment to said polyurethane in said solution is at least 1:50 and is in the range up to less than the amount of said polyurethane.

The plastic polymer in low relief is preferably deposited as a viscous pigment-containing solution thereof, by mezzo printing. The process preferably includes the further step of depositing a higher relief visible pattern of plastic polymer over said discontinuous pattern or open pattern to produce a surface having higher relief polymer masses with said low relief pattern between said masses. Thus preferably the solution is applied to, substantially the whole surface of a microporous, moisture vapour-permeable elastomeric polyurethane sheet material, to form a discontinuous pattern or an open pattern of elastomeric polyurethane in relatively low relief and then more solution is applied to form a second discontinuous pattern or an open pattern of elastomeric polyurethane in higher relief. The process of this aspect of the invention makes it possible to produce a microporous leather substitute having a desirable grain pattern which is highly resistant

to abrasion and scuffing and which has excellent moisture vapour permeability making it very suitable for uppers for men's shoes, for example.

5 The said plastic polymer in a higher relief pattern may be deposited as a viscous pigment-containing solution thereof, by intaglio printing.

10 The treated microporous sheet material may be then heat-treated at a temperature below the collapse temperature of said sheet material and within 40°C of said collapse temperature to cause said sheet material to shrink by at least 5% in area.

15 In a preferred aspect of the present invention the microporous sheet material is one which does not have its extensibility constrained by the presence of a reinforcing fabric such as a woven or non-woven fibrous fabric. Throughout its thickness it consists essentially of non-fibrous elastomeric polyurethane material. Unlike the conventional leather substitutes which have ultimate elongations of some 20-40%, it can be stretched well over 50% (e.g. well over 100% and usually well over 200%). Preferably, the sheet, suitable for making shoe uppers, has a thickness of at least 25 mils (0.63mm), e.g. 30 to 100 mils (about 0.75 to 2.5mm) and preferably 30 to 70 mils (about 0.75 to 1.8mm), e.g. 0.8 to 1.1mm for women's shoe uppers and 1.5 to 1.8mm for men's shoe uppers.

Especially suitable microporous sheets have a density above 0.3 g/cm³ (preferably in the range of 0.35 to 0.68 g/cm³, more preferably at least 0.4 g/cm³ e.g. 0.4 to 0.5 g/cm³), and are substantially free of macropores. In one form of the invention the microporous material being treated comprises a more dense base layer (e.g. of apparent density 0.4 to 0.5 g/cm³, and 0.6 to 1.6mm thick) and a less dense upper layer (e.g. of apparent density 0.3 to 0.4 g/cm³ and 0.1 or 0.2 to 0.5mm thick).

The heat treatment mentioned above is conveniently carried out in a stream of hot air, e.g. in a suitable convection oven, while the sheet material is supported horizontally on a support which permits the desired planar shrinkage, such as a grate or a series of closely spaced rollers or an endless canvas belt. When the material being treated is in the form of a continuous sheet, little if any lengthwise tension is applied in order to move the material through the oven. The sheet material may, less desirably, be hung vertically, particularly when the width of the material is not great and the force of gravity resisting shrinkage is therefore small.

Instead of heating by convection from a hot gas, the heat may be supplied by radiation (e.g. by infrared heaters or by dielectric heaters, such as those operating at radio frequencies) or by conduction, as by passing

the material over hot rolls (e.g. conventional hot "cans") or through a hot liquid medium, in such a way that the planar shrinkage occurs.

The time (duration) and temperature of the heat treatment will depend on the particular polyurethane composition; thus it should not be so high as to melt the material or cause a collapse of its pores. The time and temperature of treatment should, however, be high enough to cause an area shrinkage of above 5% e.g. in the range of 5 to 40%. The temperature of the heat treatment is preferably at least 2°C less than the collapse temperature of the microporous material, well within 40°C of the collapse temperature and usually within 30°C and often well within 15°C of it (e.g. 5—15°C less than the collapse temperature). The duration of the heat treatment is preferably relatively short, well below an hour, and usually well below 15 minutes. The optimum temperature and duration of treatment can be determined by simple experimentation and will of course depend in part on the efficiency at which the heat is transferred to and through the surface zones of the microporous material (which is itself a heat-insulating structure). Generally in a convection oven the duration is over a minute, e.g. 3 to 5 minutes. The measurements of temperature in a convection oven are conveniently made by placing a thermocouple in the air very close to (i.e. just above) the upper surface of the sheet material.

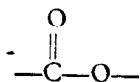
In one particularly preferred process, little if any change in the thickness of the material is observed during the heat treatment. In another embodiment, which is especially suitable when the microporous structure, prior to heat treatment, is of low density, e.g. 0.2—0.3 g/cm³ the treatment is such as to cause substantial decrease in thickness and consequent greater densification, e.g. to provide a material having a density above 0.35 g/cm³ (such as 0.35 to 0.5). A treatment under conditions to reduce thickness may also be employed to make acceptable for certain uses an otherwise unacceptable sheet; for instance a material 1.1mm in thickness, which is too thick for use in place of the upper leather in ladies' lined shoes (although acceptable for other uses) may be heat treated to reduce its thickness to an acceptable 0.8mm. Preferably the sheets are substantially free of visible pores (macropores) both before and after the heat treatment.

The heat-treated microporous sheet preferably has an apparent density in the range of 0.35 to 0.7, and more preferably in the range of 0.4 to 0.5 or 0.6 grams/cm³. The specific degree of shrinkage occurring during heat treatment depends in part on the structure of the material and its previous history. The apparent density of the microporous sheet before heat treatment is preferably

below 0.5 or 0.6 e.g. in the range of 0.35 to 0.55, grams/cm³. Typically the density of the polyurethane itself is about 1.2 grams/cm³; it will therefore be apparent that in the neighbourhood of 1/4 to 1/2 of the volume of the microporous material is air.

The solid polymeric material of the microporous sheets treated in accordance with this invention is a thermoplastic elastomeric polyurethane material having an intrinsic viscosity of above 0.6, preferably 0.8, and more preferably 1 or more. The polyurethane is composed of segments having urethane linkages and intermediate longer segments which may be for example of polyester or polyether character. The urethane linkages are preferably derived from diisocyanates, such as diphenyl methane p, p'-diisocyanate, and are thought to provide so-called "hard" segments in the polymer molecule, while the other segments (e.g. the polyester or polyether segments) are flexible or "soft". Polyurethanes of this type are known in the art. They may be made, for instance by reacting a relatively low molecular weight hydroxyl-terminated polyester or polyether (e.g. of molecular weight below 6000, and preferably between 800 and 2500) with a low molecular weight glycol and a diisocyanate.

In making the polyurethane one may employ a polyester of a hydroxycarboxylic acid (e.g. a polycaprolactone) or a polyester of a glycol and a dicarboxylic acid (e.g. ethylene glycol adipate or 1,4-butanediol adipate) or a mixed polyester of these types of components. Examples of other dicarboxylic acids which may be used instead of, or in addition to, adipic acid, are succinic, pimelic, suberic, azelaic or sebacic acids or aromatic acids such as phthalic acid or terephthalic acid. Examples of other glycols which may be used to make the polyester are 1,6-hexanediol and 1,8-octanediol. The most useful polyesters are aliphatic polyesters in which the



groups are separated by aliphatic chains averaging 3 to 6 carbon atoms in length.

Typical polyethers which are used to provide the soft segments for elastomeric polyurethanes are usually of aliphatic character. One type has the formula H (RO)_nH where R is a divalent alkylene radical, such as tetramethylene or ethylene or propylene, and "n" denotes the degree of polymerization.

The preferred diisocyanate is diphenyl methane p, p'-diisocyanate but other diisocyanates may be used as such or in admixture therewith. Examples of other diisocyanates are 2,4-toluene diisocyanate, p,p'-

diphenyl diisocyanate and tetramethylene diisocyanate.

The low molecular weight glycol referred to above acts as a chain extender. The preferred chain extender is tetramethylene glycol, but other chain extenders may be used as such or in admixture therewith. Examples of such other difunctional chain extenders are other dihydric alcohols such as ethylene glycol, hydroxy amines such as 2-aminoethanol, diamines such as ethylene diamine, or water. The amount of chain extender is preferably such as to produce a thermoplastic product of high intrinsic viscosity.

In the preferred class of polyester polyurethanes made with diphenylmethane-p, p'-diisocyanate, those having nitrogen contents in the range of 4 to 5%, most preferably in the neighbourhood 4½%, (e.g. 4.4—4.6%) have been found to be particularly suitable.

For best results, the polyurethane material used to make the microporous sheet should have a melting point of at least 100°C preferably above 150°C, e.g. about 170 to 200°C (as measured by differential thermal analysis or differential scanning calorimetry). When formed into a smooth void-free thin film 0.2—0.4mm in thickness it should, for best results, have the properties described below; such thin films can be formed by careful casting of solutions of the polymer (e.g. a degassed 30% solution in dimethylformamide) followed by careful evaporation of the solvent in a dry atmosphere; a tensile strength of at least 210 kilograms per square centimeter (preferably at least 350, e.g. 420 to 560), a percent elongation at break of at least 300% (preferably at least 400, e.g. 500 to 700%), an elastic modulus of at least 105 kilograms per square centimeter (preferably at least 350 e.g. 560 to 770), a 100% secant modulus (stress divided by strain at 100% elongation) of at least 28 kilograms per square centimeter (preferably at least 84, e.g. 110 to 134). These mechanical properties are measured by ASTM D832-67.

The polyurethane (again, tested as a thin film made as described above) should recover completely from a 5% elongation at room temperature (23°C) but preferably does take on a permanent set (one measured for example as in an ASTM D412-66) after a 100% elongation. This set is usually within the range of 5 to 20%; for the best materials thus far employed it is in the range of 10 to 20% e.g. about 15%. A typical material shows a tension set of some 24—26% immediately on release of the clamps after being held at the 100% elongation for 10 minutes while the "permanent set", which is here taken as the tension set measured 1 hour after the release of the clamps, is 14% (measured on a film specimen 1cm wide with a gauge length of 5cm and a strain rate, for the 100% elongation, of 24% per minute). Pre-

ferably the material has a Shore hardness of at least 75A (more preferably about 90A to 69D), measured by ASTM D1706-67.

The polyurethane material may be composed of polyurethane *per se*. It is also within the broad scope of the invention to use polyurethane materials which are blends of polyurethane and other high polymers such as a vinyl chloride polymer (e.g. the vinyl chloride copolymers known as Bakelite (R.T.M.) VYHH or VAGH, containing vinyl acetate as a comonomer) or a rubbery copolymer of a conjugated diolefin and acrylonitrile (e.g. the butadiene-acrylonitrile copolymer known as Hycar (R.T.M.) 1031). The amount of such other high polymer is generally below 40% (e.g. 10% to 20%) of the total weight of the blend.

The preferred thermoplastic elasomeric polyurethanes are understood to have few, if any, chemical cross links and are believed to derive their properties primarily from hydrogen bonding forces rather than cross linkages. Their stress-strain curves are of the same general shape as those shown in Figure 1 of the article by Stetz and Smith in Rubber Age, May 1965 page 74. While the polyurethane itself usually shows a tension set below 100%, as previously discussed, the preferred microporous polyurethane sheets generally recover completely with substantially no permanent set (under standard dry conditions at room temperature) after being stretched 100%.

The heat-treated microporous sheet preferably has a percent elongation at break of above 50% (e.g. above 100% or 150%, such as in the range of 300 to 400% or more); a tensile strength above 35 Kg/cm² (e.g. in the range of 60 to 100); an elastic modulus above 2 Kg/cm² (e.g. in the range of 4 to 9), and a slit tear strength (ASTM D2212-64) above 1 Kg per mm thickness (e.g. in the range of about 2 to 5). Desirably the microporous sheet, before heat treatment, should have a percent elongation at break above 50%, more preferably 70% or higher and a tensile strength of at least 5 Kg/cm². Both before and after the heat treatment it should permit the passage of water vapour (thus its water vapour transmission should be at least 200 g/m²/24 hrs (measured as in ASTM E 96-66, procedure B).

The "microporous" materials used in the process of this invention have pores invisible to the naked eye of a person with 20/20 vision. Such pores measure less than 100 microns in their maximum dimension (when a plane surface, such as the top or bottom of the material or a cross-section thereof is observed). As will be seen hereafter, the pores generally measure well below 50 microns in their maximum dimension.

The invention can be put into practice in various ways and a number of specific

embodiments will be described by way of example with reference to the accompanying drawings, in which:—

Figure 1 is an enlarged photomicrograph looking down at the upper surface of a sheet made according to the invention,

Figure 2 is a view like Figure 1 but at a higher magnification,

Figure 3 is an enlarged photomicrograph looking down at an engraved "mezzo screen" printing plate used for applying the low relief pattern,

Figure 4 is an enlarged photomicrograph looking down at an intaglio printing plate used for applying the high relief pattern, and

Figure 5 is a photomicrograph of a cross-section taken through the upper portion of a microporous sheet material before treatment according to this aspect of the invention.

Figures 1 to 5 relate to an embodiment in which the solution is applied by two printing steps, a low relief printing followed by a higher relief printing.

In each of the Figures the scale of the photomicrograph is shown.

The drawings shown in Figures 1, 2 and 5 are derived from photomicrographs obtained with a scanning type electron microscope (Type JSM, Japan Electron Optics Laboratory Co., Ltd.), viewing cross-sections of the sheet material (obtained by cutting perpendicularly through the thickness of the sheet with a razor). In preparation for viewing the cut sheet material is given a very thin uniform metallic (gold-palladium) coating about 300 Angstroms in thickness; the coating may be applied by evaporating the metal onto the specimen in a high vacuum (e.g. 10⁻⁴ mm Hg absolute), the specimen being rocked while metal deposition is occurring, so as to distribute the metal uniformly over the surface, including the crevices, of the specimen. This coating serves to conduct away the electron charge which would otherwise accumulate on the surface of the specimen when it is exposed to the electron beam in the scanning electron microscope. The approximate scale is indicated for each photomicrograph. In viewing the photomicrographs it should be borne in mind that the scanning type electron microscope has a great depth of focus (nearly 300 times that of the light microscope) such as about 300 microns at 100X magnification or 100 microns at 1000X magnification, enabling one to, in effect see into the interiors of the pores.

In the microporous sheet shown in Figure 5 the pore system comprises cavities 42 having their maximum dimensions in the range of up to about 45 microns connected by passages which may have much smaller dimensions (e.g. maximum dimensions apparently as low as about ½ micron). The walls of the cavities may be very thin, e.g. within the range of about 1 to 10 microns. Fine cavi-

ties may also be present in the walls of the irregular cavities. One suitable method for making such a structure is by forming, as on a temporary support, which is preferably liquid permeable, a thick layer of a mixture of a leachable material (such as microscopic sodium chloride particles) and a solution of the thermoplastic polyurethane in a solvent (e.g. dimethylformamide) and treating the layer adhering to the support with a liquid coagulant-leaching agent (e.g. water) which is a non-solvent for the polyurethane and at least partially miscible with the solvent, so as to coagulate the polyurethane into a microporous sheet; the treatment with the coagulant is continued until substantially all the solvent and leachable material are removed; the resulting water vapour-permeable flexible sheet material is dried and stripped from the temporary support at any stage after the polyurethane has been coagulated to self supporting form.

The microporous sheet material to be treated in accordance with this invention is preferably coloured, at least at its upper surface. To this end the polyurethane material forming the sheet may contain a small amount of pigment (e.g. carbon black) or the sheet may be dyed with a solution of a solvent dye (such as an "Irgacet", (R.T.M.) dye, which may be of the type described in U.S. Patent 2,551,056, dissolved in methanol).

As indicated previously, it is preferred to start with a microporous polyurethane sheet having a coloured upper surface. The colour may be imparted to the sheet material by including a small amount of a pigment (e.g. 1 to 5% of carbon black or other black, brown, or other coloured pigment material) in intimate admixture with the polyurethane (or polyurethane precursor, when employed) prior to the formation of the sheet therefrom. Alternatively, the colour may be imparted to the sheet by a dye which may be applied subsequent to the making of the sheet. One suitable process for dyeing is by applying a solution of the dye in a volatile organic solvent; dyes such as those known as Irgacet dyes made in accordance with U.S. patent 2,551,056 (e.g. premetallized monoazo dyes, such as Irgacet Black RL or Irgacet Brown 2GL) dissolved in methanol may be used. The dye may be applied to a pigmented or unpigmented sheet. The dye or pigment may be present only in the upper surface zone of the sheet material, or may be present in higher concentration in said surface zone than in the rest of the sheet, or may be present more or less uniformly throughout the sheet. The upper surface of the dyed or pigmented sheet preferably has a relatively uniform overall appearance, though it may have some streakiness owing, for instance, to difficulties in obtaining absolutely uniform

dyeing or in obtaining an absolutely uniform surface on the sheet material.

Another type of microporous sheet which may be treated in accordance with this invention has a structure in which the pore system is substantially free of the larger cavities seen in Figure 5, but instead includes a multitude of fine interconnected pores of considerably smaller size. One technique for making such a product uses a mixture comprising the thermoplastic elastomeric polyurethane uniformly distributed in a blend of a volatile solvent and a miscible less volatile nonsolvent. In a preferred version of this technique a clear hot solution of the polyurethane in the solvent-nonsolvent blend is cooled until a cloudy colloidal dispersion of the polyurethane is formed; this cloudy dispersion is cast as a thick layer onto the temporary support and the solvent and non-solvent are evaporated, and the sheet is removed from the support.

Microporous sheets which may be treated in accordance with the present invention may be made by other techniques. Thus, other coagulating methods may be used to treat the thick layer of the mixture of polyurethane solution and leachable material. Among such coagulating methods are cooling the mixture, (e.g. -78°C), or subjecting the mixture to vapours of non-solvent (e.g. to a humid atmosphere), or simply evaporating the solvent, preferably at a rate slow enough to avoid the formation of macroporous bubbles or holes in the sheet, or using various combinations of these coagulating methods (e.g. freeze drying techniques) before removal of the leachable material (e.g. NaCl) or other microscopic particular material. In place of, or together with, the salt particles, other pore-forming microscopic particulate material may be used. These particulate materials may be starch particles (which may be removed by treating the coagulated layer with an aqueous starch-digesting agent, such as an enzyme, of known type). Or they may be other microscopic solid particles which are insoluble in the polyurethane solution and which can either be dissolved out by treating the coagulated sheet with water or other suitable solvent for the particle which is a non-solvent for the polyurethane or can be otherwise destroyed or removed; examples of such particles are sodium carbonate, oxalic acid, ammonium carbonate, or suitable microballoons. Alternatively, the void-forming particulate material may be in the form of dispersed microscopic droplets of a liquid insoluble in the solution of polyurethane or in the form of dispersed microscopic bubbles of gas. The particle size of the microscopic particulate material is well below 100 microns preferably less than 50 microns and greater than about one micron, more preferably in the range of about 3 to 20 microns. The

ratio of the total volume of the microscopic particulate void forming material and the total volume of polyurethane in solution may be for instance, in the range of 0.5:1 to 5:1, preferably in the range of 1:1 to 3:1, thus 178 grams of the sodium chloride particles may be mixed with 333 grams of a 30% solution of the polyurethane in dimethyl-formamide, giving a volumetric salt:polymer ratio of 1:1.

It is also within the broad scope of this invention to employ microporous materials made by a process in which fine particles of the polyurethane, with or without a particulate void-forming material (such as any of the microscopic particulate materials previously mentioned), are fused together at their points of contact as by means of heat alone or heat in the presence of a solvent or swelling agent for the polymer which solvent or swelling agent may be distributed over the surfaces of the polymer particles, followed, when desired, by removal of any of the void forming particulate material that may be present.

In one preferred embodiment the thermoplastic polyurethane material present in the solution is of substantially the same type as that constituting the microporous sheet. It may also be desirable to use for this purpose a polyurethane made from an aliphatic diisocyanate, such as hexamethylene diisocyanate or tetramethylene diisocyanate, giving a polyurethane which is itself substantially free of discolouration and resistant to oxidation and development of colour. An antioxidant and/or a stabilizer against deterioration by ultraviolet light may also be included in the spraying solution.

The invention is most useful in making substitutes for shoe upper leather. In the manufacture of shoes, it is customary to cut the upper leather, usually with a die by machine, and to fit and assemble the parts of the upper together (including any doubler or lining that is to be used) as by stitching and/or cementing so as to ready the upper for lasting. After the insole has been secured to the bottom of the last, the upper is placed on the last, pulled over the wooden last so as to conform tightly to it, and attached to the insole. This "pulling over" is generally effected by mechanisms which grip, and pull, the upper at its edges, e.g. at the toe and sides.

During the fitting together of the upper, the edges of the upper leather are generally "skived", by cutting a bevel on the "flesh side" of the leather adjacent its edge and the skived edge is then cemented, folded back on itself and pressed in place, to give a neat finished top line or other edge.

Descriptions of the conventional methods for making shoes are contained in the 61 page publication "How American Shoes Are

Made" 3rd edition, copyright 1966 by United Shoe Machinery Corporation.

Excellent men's and women's shoes have been made with materials produced in accordance with this invention in place of the usual upper leather. The upper not only conforms unusually well to the last, without wrinkling or puckering, but also retains its lasted shape very well after removal from the last, particularly when the upper has been given the conventional type of heat setting treatment (e.g. setting with heat alone or moist heat) on the last. The material has very good skiving characteristics, particularly if it is wet with water prior to skiving. The shoes are comfortable and the uppers show very good wear resistance. Unlike many shoes made with the conventional fabric-reinforced leather substitutes, there is no problem of fabric show-through or orange peel on lasting.

The following Example is given to illustrate this invention further. In the Example all pressures are atmospheric unless otherwise indicated. In the application all proportions are by weight unless otherwise indicated.

A microporous elastometric polyurethane sheet, product A, 1mm thick and weighing about 510 grams per square meter is made from a polyester polyurethane prepared by reacting Desmophen (R.T.M.) 2001 polyester (a hydroxyl-terminated polyester of 2000 molecular weight made from 1 mol butane diol-1,4, 1.13 mol ethylene glycol and 2 mols adipic acid), 1,4-butane-diol (as a chain extender), diphenylmethane - p,p' - diisocyanate, and methanol (as a chain terminator), all dissolved in N,N-dimethyl-formamide ("DMF") under such conditions and in such proportions as to produce a 30% solution of an unreactive polyester polyurethane have an intrinsic viscosity of 1.0 (measured in DMF) a polyester content of 50.3% and a nitrogen content of 4.4%.

In the manufacture of the microporous material the polyurethane solution is mixed with micropulverized sodium chloride in a ratio of 1.78 parts of salt per part of polyurethane, the solution is degassed cast on a porous temporary support, to which it adheres and immersed in water to coagulate the cast layer and to extract the salt and then dried and removed from the temporary support as by stripping it from the support.

Alternatively the microporous material may be a two-layer material about 2mm thick, product B, made in a manner similar to that of product A except that two mixtures of different salt contents (salt: polymer ratios of 1.78:1 and 3:1) are cast, one on top of the other (with the material of higher salt content on top) onto the porous temporary support and the whole cast material is immersed in the water to coagulate the poly-

urethane and extract the salt. The two layers have a similar appearance when viewed in cross section with the electron scanning microscope, but the proportion of voids is of course, higher in the upper layer. The less dense upper layer is about 0.4mm thick. The density of the two layer sheet is about 0.412 g/cm³.

These two alternative materials A and B can be used to produce the product illustrated in the drawings.

A indicated, the invention has its greatest utility in the treatment of unreinforced microporous polyurethane elastomer sheet material. In its broader aspects, however, the invention may be applied to microporous sheets which comprise a woven or non-woven fabric backing coated with, and usually impregnated with, microporous polyurethane elastomer material. In this case the microporous layer overlying the impregnated fabric layer is usually relatively thin, e.g. below 25 mils (0.63mm) e.g. 0.2 to 0.4mm) although the total thickness of the sheet material (including the fabric body layer or reinforcement) is about the same as that of the applicant's preferred unreinforced polyurethane sheet material. In one embodiment, there may be formed on the fabric base layer a microporous layer of polyurethane material having a relatively low apparent density (e.g. a layer 0.5mm thick having an apparent density of 0.3 or 0.4 g/cm³).

EXAMPLE

As indicated in Figures 1 and 2 the upper surface of the sheet carries spaced masses 32 of elastomeric polyurethane and also carries an open pattern of thin irregular-shaped lines, or low ridges, 33 of thermoplastic elastomeric polyurethane, in the spaces between masses 32. In the illustrated embodiment these ridges, as such, form a continuous network and the ridges cover about 60% of the total projected surface area of the spaces between the masses 32; the spaces between ridges in turn represent, correspondingly, about 40% of that total projected surface area. The widths of the illustrated ridges 33 are of the order of 0.25 to 1.0 mils (0.006 to 0.025mm) and their heights are less than one mil and over 1/10 mil, being of the order of $\frac{1}{4}$ to $\frac{1}{2}$ mil (0.006 to 0.012mm). It will be seen that no point in the pattern is more than 2 mils from a ridge (or mass). In the preferred embodiment the heights of the masses 32 are at least 50% greater than the heights of ridges (e.g. 2, 3, 5 or 6 times the heights of the ridges).

The upper surface of the sheet, and the ridges 33 and the masses 32 may be of the same colour or contrasting colours. Thus a sheet which has been dyed brown may carry black ridges and brown masses, giving a two-tone, or "aniline" effect. An undyed sheet

(of white appearance) may be similarly treated or it may have a pattern of white ridges and blue masses, or orange ridges and green or blue masses, or any other desired combination of different colours or tones.

The overall appearance is somewhat similar when the product does not contain the low relief pattern in the areas between the masses 32, but the abrasion resistance of the product is considerably lower.

The illustrated product is produced by a method in which the ridges 33 are deposited on the upper surface of the sheet 31 in an overall pattern (a so-called Mezzo Screen pattern, as shown in Figure 3) and the masses 32 are then deposited thereover in the indicated pattern, so that the pattern of ridges is now visible only in the areas between the masses, the other ridges having been merged into the masses 32 covering them.

The ridges 33 and masses 32 may be formed on the sheet by intaglio printing operations, using a relatively viscous solution of a thermoplastic elastomeric polyurethane in a volatile solvent, which solvent is also a solvent for the polyurethane material of the base sheet, aiding in the bonding together of the deposited ridges, masses and base surface. This viscous solution is pigmented. It may be placed on the intaglio printing plate (Figures 3 and 4) and doctored (as with a steel doctor blade) into the engraved areas of the plate so that it fills the engraved areas and is removed from the unengraved portions. The upper surface of the sheet is then brought into contact with the printing plate and pressed against it with sufficient pressure to transfer the solution from the engraved portions to the sheet; such pressure may be applied in conventional manner, as by means of a rubber surfaced roll passing against the back of the sheet. The printed sheet may be then treated to remove the solvent, as by passing it through a hot air oven.

One suitable solution for use in the mezzo screen printing comprises 20% of the polyurethane described above for product A dissolved in a dimethylformamide and containing 20% dispersed carbon black.

One suitable solution for use in the intaglio printing has the following composition: 20 parts of thermoplastic elastomeric polyurethane (e.g. Estane (R.T.M.) 5707 which is substantially the same as the Estane 5740X7 described by Stetz and Smith in Rubber Age, May, 1967, Pages 74—79) 2 parts of pigment (e.g. Excelsior Carbon Black of Columbia Carbon) and 78 parts of dimethylformamide (i.e. N,N-dimethylformamide). Because the solvent is removed after deposition of the solution, one deposits the solution as a ridge or mass of greater thickness than that of the final dried ridge or mass. Correspondingly the depths of the engraved portions of the

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printing plate are greater than the heights of the ridges and masses. Thus, for the particular solution described above, intaglio printing plates having engraved portions whose depths are about $1\frac{1}{2}$ mils (about 0.04mm) and about 5 mils (about 0.13mm) yield dried ridges and masses whose heights are about 0.4 mils (about 0.01mm) and about $1\frac{1}{2}$ -2 mils (about 0.04—0.05mm), respectively.

These heights will also depend in part on the character of the surface being treated. For instance, for a low density, highly soluble, highly porous surface a more viscous polymer solution having a lower solvent activity with respect to the surface may be needed to accomplish the same results.

Pigments of various types may be present in admixture the solution being printed. These may be, such materials as carbon blacks (e.g. Excelsior or Raven II carbon blacks of Columbia Carbon), Phthalocyanine Blue BT 284 D, Phthalocyanine Green GT 674 D, Monastral Red RT 790 D, Chloride White R900, Monastral Scarlet RT 7870, of Vat Yellow 212896 or mixtures of pigments.

It is preferred that the low relief material (e.g. the ridges 33) occupy 30 to 60% of the projected area of the spaces between the high relief masses, that the height of the low relief material be in the range of $\frac{1}{4}$ to 1 mil, while the high relief masses occupy 20 to 70% of the total projected area of the surface of the sheet and their heights are in the range of about $\frac{1}{2}$ to $1\frac{1}{2}$ mils. The moisture vapour permeability (MVT) of the product is preferably at least $1\text{g}/30\text{cm}^2/24$ hrs. (measured at 70°F and 50% R.H.) and at least one half of that of the base sheet; for one typical sheet the MVT of the base sheet was originally $2\text{g}/30\text{cm}^2/24$ hrs. and its MVT after printing in accordance with this invention was $1.6\text{g}/30\text{cm}^2/24$ hrs.

The material retains the good flex life of the original base sheet (i.e. it has good resistance to the formation of outfold cracks during cold flex testing according to ASTM D2097-62T on a Newark Leather Finish Co. flex testing machine operated in an atmosphere at a temperature of 0°C).

Excellent results have been obtained by using elastomeric polyurethanes as the material for both the high relief and low relief patterns. It is within the broader scope of this invention however to use other materials for one or both of these patterns. Examples of such other materials are vinyl or acrylic resins, such as plasticized polyvinyl chloride, polyvinyl butyral, polymers and copolymers of alkyl acrylates, or epoxy resins.

It is within the broader scope of the invention to make a material of little grain, or more uniform (and less marked) grain by depositing only the discontinuous or open

pattern in low relief. This can be done with a single low-relief printing as described or with two or more such printings so as to deposit successive low-relief patterns out of registry with each other, so that the low relief patterns cover, say, 30 to 70% of the projected area of the sheet. While the resulting sheet does not have the pronounced grain it does have good abrasion resistance, moisture vapour permeability and flex life.

WHAT WE CLAIM IS:—

1. A flexible water-vapour permeable sheet material having a microporous surface of elastomeric polyurethane carrying on its surface a discontinuous pattern or an open pattern of plastic polymer containing pigment in low relief, said pattern being such that no point in said pattern is further than 2 mils from the boundary of a relief deposit of plastic polymer, and the height of the low relief pattern is not more than 1 mil.

2. A sheet material as claimed in Claim 1 in which said deposited low relief polymer occupies 30 to 70% of the projected area of said pattern.

3. A sheet material as claimed in Claim 1 or Claim 2 in which the sheet carries also a higher relief pattern of spaced masses of plastic polymer with said low relief pattern being situated between said masses.

4. A sheet material as claimed in Claim 1, 2 or 3 in which the said plastic polymer is a thermoplastic elastomeric polyurethane.

5. A sheet material as claimed in Claim 3 or Claim 4 in which the low relief pattern occupies 30% to 60% of the projected area of the spaces between the high relief masses and the height of the low relief pattern is in the range 0.25 to 1 mil and the high relief pattern occupies 20% to 70% of the total projected area of the sheet and the height of the high relief pattern is in the range 0.4 to 2.0 mils.

6. A process for the production of a sheet material as claimed in Claim 1 which comprises treating a surface of a flexible sheet material which surface consists essentially of preformed solid water vapour permeable microporous thermoplastic elastomeric polyurethane material optionally containing up to 20% by weight of other thermoplastic elastomeric polymer by contacting said surface locally with a discontinuous pattern or, an open pattern of a solution of an elastomeric polymer containing dispersed pigment in a solvent for said polyurethane of said surface said solution containing at least 1% by weight of polyurethane in such a way that there is deposited on the said surface a discontinuous or an open pattern of plastic polymer in low relief, and drying to remove the solvent by evaporation, said pattern being such that no point in said pattern is further than 2 mils from the boundary of a low relief deposit of

- said polymer, and the height of the said low relief pattern is not more than 1 mil.
7. A process as claimed in Claim 6 in which the solution of elastomeric polymer comprises a solution of an elastomeric polyurethane-containing dispersed pigment in a solvent for said polyurethane of said surface said solution containing from 1% to 20% by weight of polyurethane and the amount by weight of said pigment to said polyurethane in said solution is at least 1:50 and is in the range up to less than the amount of said polyurethane.
8. A process as claimed in Claim 6 or Claim 7 in which the plastic polymer in low relief is deposited as a viscous pigment-containing solution thereof, by mezzo printing.
9. A process as claimed in Claim 6, 7 or 8 and including the further step of depositing a higher relief visible pattern of plastic polymer over said discontinuous pattern or open pattern to produce a surface having higher relief polymer masses with said low relief pattern between said masses.
10. A process as claimed in any one of Claims 6 to 9 the said deposited low relief polymer occupies 30 to 70% of the projected area of the said pattern.
11. A process as claimed in any one of Claims 6 to 10 in which the said plastic polymer in a higher relief pattern is deposited as a viscous pigment-containing solution thereof, by intaglio printing.
12. A process as claimed in any one of the preceding Claims 6 to 11 in which the treated microporous sheet material is then heat-treated at a temperature below the collapse temperature of said sheet material and within 40°C of said collapse temperature to cause said sheet material to shrink by at least 5% in area.
13. A process of making a sheet material as claimed in Claim 6 and as specifically described herein with reference to the Example.
14. A sheet material when made by a process as claimed in any one of Claims 6 to 13.
15. A sheet material as claimed in Claim 1 and substantially as specifically described herein with reference to Figures 1 and 2 of the accompanying drawings.

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SPECIFICATION NO 1325850

In accordance with the Decision of the Principal Examiner, acting for the Comptroller-General, dated 17 August 1976 this Specification has been amended under Section 31 in the following manner:-

Page 3, *delete* lines 99 to 108

Page 8, line 109, *delete* 6 *insert* 5

Page 9, lines 3 and 43, *delete* Claim 6 *insert* Claim 5

Page 9, lines 14 and 15, *delete* Claim 6 or Claim 7 *insert* Claim 5 or Claim 6

Page 9, lines 18 and 19, *delete* Claim 6, 7 or 8 *insert* Claim 5, 6 or 7

Page 9, line 26, *delete* Claims 6 to 9 *insert* Claims 5 to 8

Page 9, line 30, *delete* Claims 6 to 10 *insert* Claims 5 to 9

Page 9, line 35, *delete* Claims 6 to 11 *insert* Claims 5 to 10

Page 9, line 46, *delete* Claims 6 to 13 *insert* Claims 5 to 12

Page 9, *for* Claims 7 to 15 *read* 6 to 14 inclusive

THE PATENT OFFICE
14 September 1976

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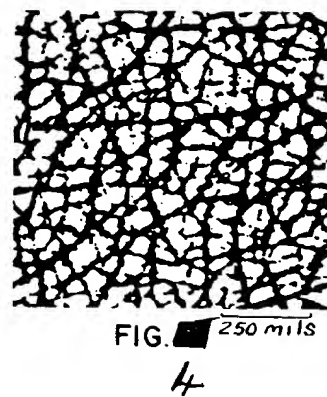
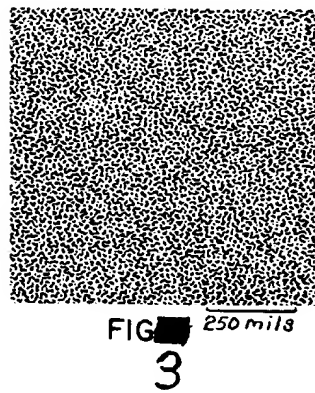
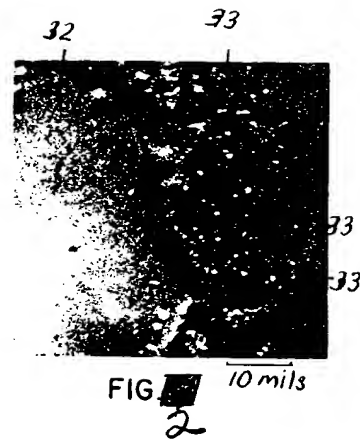
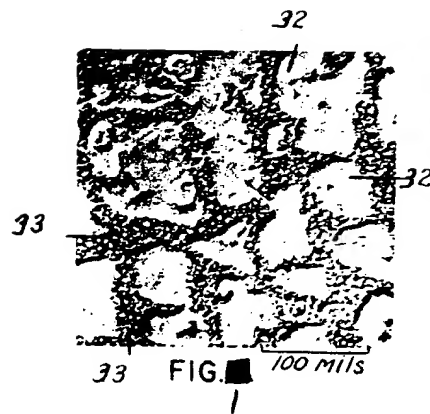
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COMPLETE SPECIFICATION

2 SHEETS

*This drawing is a reproduction of
the Original on a reduced scale*

Sheet 1



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COMPLETE SPECIFICATION

2 SHEETS

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Sheet 2

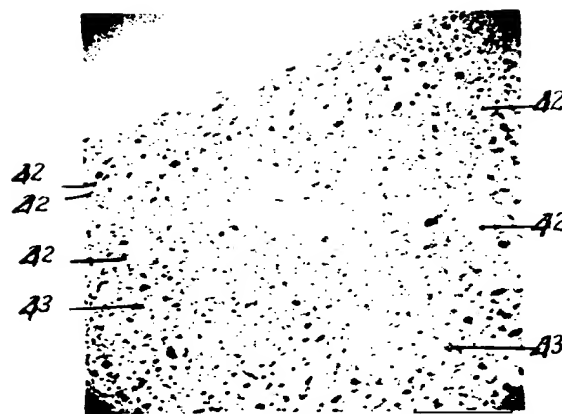


FIG 5

250 MICRONS

